TOPIC 06 – KINETICS
6.2A: COLLISION THEORY
6.2B: MAXWELL-BOLTZMANN & CATALYSTS

IB Chemistry

T06D03/4

6.2 Collision theory - 3 hours

- 6.2.1 Describe the kinetic theory in terms of the movement of particles whose average energy is proportional to temperature in kelvins. (2)
- 6.2.2 Define the term activation energy, Ea. (1)
- 6.2.3 Describe the collision theory. (2)
- 6.2.4 Predict and explain, using the collision theory, the qualitative effects of particle size, temperature, concentration and pressure on the rate of a reaction. (3)
- 6.2.5 Sketch and explain qualitatively the Maxwell–Boltzmann energy distribution curve for a fixed amount of gas at different temperatures and its consequences for changes in reaction rate. (3)
- 6.2.6 Describe the effect of a catalyst on a chemical reaction. (2)
- 6.2.7 Sketch and explain Maxwell– Boltzmann curves for reactions with and without catalysts. (3)


sandman117
collect and combine
collision theory

6.2.1 – Kinetic Theory

- 6.2.1 Describe the kinetic theory in terms of the movement of particles whose average energy is proportional to temperature in kelvins. (2)
- Temperature is directly related to the kinetic energy of particles.

6.2.1 – Assumptions for KMT

- The kinetic theory (often used interchangeably with the collision theory or kinetic molecular theory) assumes the following:
  - Gas is made of very small particles with non-zero mass
  - Gases constantly move in random manner
  - The # molecules in a gas is large enough for comparison
  - Gas particles are spherical and perfectly elastic
  - Collisions with the container are perfectly elastic
  - Volume is large enough for significant space between mc's
  - Assumption that any relativistic or quantum-mechanical effects are negligible, and that any effects of the gas particles on each other are negligible, except those by collisions
  - Temperature is the only factor affecting the average KE

6.2.2 – Activation Energy

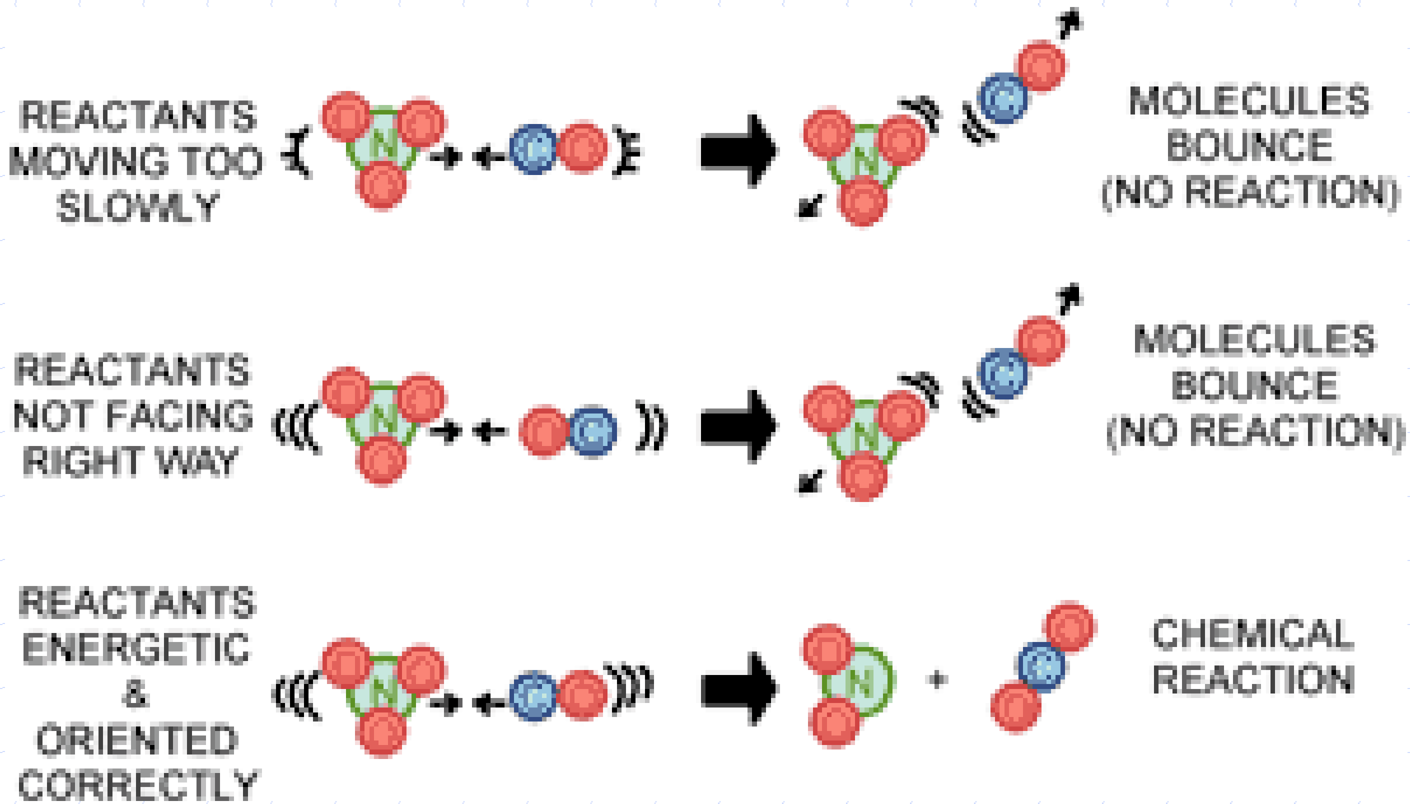
- 6.2.2 Define the term activation energy, Ea. (1)
- 6.2.3 Describe the collision theory. (2)

6.2.3 – Collision Theory

- Simple **collision theory** states that before a chemical reaction can occur, the following requirements must be met:
  - Reactants (ions, atoms, mc) must physically collide and come into direct contact with each other
  - Molecules must collide in the correct relative position so active functional groups are aligned. Overcoming **steric factors** is known as **collision geometry**.
  - Each of the particles must be traveling at sufficient velocity so that enough kinetic energy is provided when the collide for the reaction to occur. This energy barrier is known as the **activation energy**

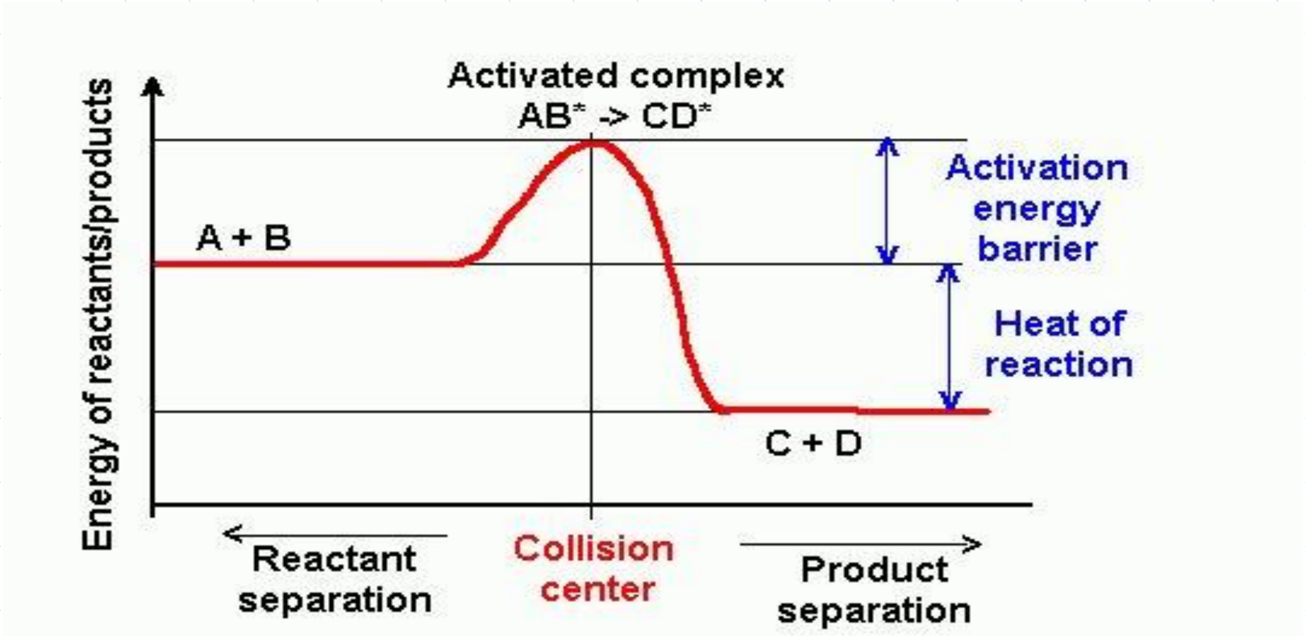
6.2.3 – In order for a collision…

- In order for a reaction to occur, the molecules must be able to overcome the energy barrier and have proper collision geometry



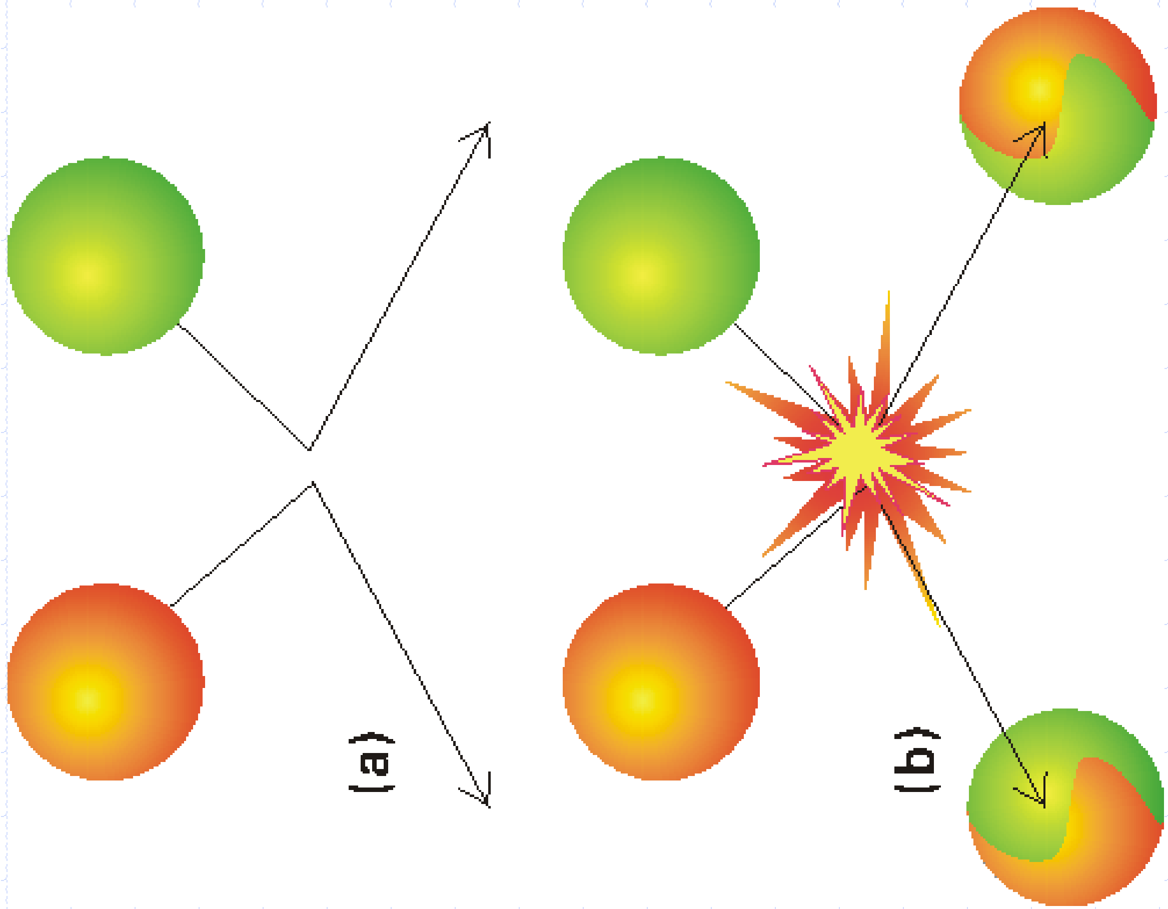
6.2.3 – Activation Energy

- Values of activation energy, E_a, vary widely between chemical reactions and control how rapidly reactions take place.
- Most reactions involve a number of steps, so E_a best corresponds to individual elementary steps



6.2.3 - Collisions

- If the reactants have enough energy, they will collide and react



6.2.3 – Relative E_a values

- Fast reactions are associated with low values of energy barriers (E_a)
- Slow reactions are associated with high values of energy barriers (E_a)
- If the colliding species do not possess sufficient kinetic energy to surmount the energy barrier and/or the correct collision geometry then an ineffective collision will occur and the reacting species will not undergo a chemical reaction.

6.2.4 – Effects on Rate of Reaction

- 6.2.4 Predict and explain, using the collision theory, the qualitative effects of particle size, temperature, concentration and pressure on the rate of a reaction. (3)

6.2.4 – Effect of Concentration

- The concentration describes the numbers of particles (usually ions in solution) in a particular volume of solution
  - ______________
- It's *generally* found that the greater the [C] of reactants, the greater the reaction rate
  - Due to increasing collisions as there are more to collide
  - *Generally* doubling the [C], doubles the rate
  - Explains why the greatest reaction rates are as soon as reactants are mixed = higher [C]

6.2.4 – Effect of Pressure

- When one or more of the reactants are gases, the pressure can lead to an increase in rate of reaction
- Increased pressure forces the molecules together for more collisions
- An increase in pressure for a gas is regarded as an increase in 'concentration' since more gas molecules are present in a particular volume of space
- Liquids and solids are affected very little by changes in pressure

6.2.4 – Effect of Temperature

- When the temperature of any particle (regardless of state of matter) is increased, it moves faster.
- This has two consequences:
  - Particles travel greater distance in a given time and so will be involved in more collisions
  - More importantly, at higher T's a larger proportion of the colliding species will have kinetic energies equal to or exceeding the energy barrier
  - Often, a rise of 10^{o}C doubles the reaction rate
    - This does not hold true for all reactions

6.2.4 – Effect of Particle Size

- When one of the reactants is a solid, the reaction takes place on the surface of the solid
- If the solid is broken up into smaller pieces or particles, the surface area is increased, giving a greater area for collisions to occur
- Several important industrial catalysts are solids and the reactions occur on the surface of the catalyst

6.2.4 – Effect of Light

- Many particles are light sensitive and increase in reaction rate when exposed to light (often UV)
- Silver halides, silver nitrate, hydrogen peroxide, and nitric acid are all **photosensitive** and undergo partial decomposition (to form radicals•) in the presence of sunlight
  - What's a radical? A radical (ex. NO•) is an unpaired electron which is therefore fairly reactive (you will see in Organic and Environmental Chemistry)
  - This is why hydrogen peroxide is stored in a dark brown bottle to keep the light out!

Factor	Reactions affected	Change made in conditions	Usual effect on the initial rate of reaction
Temperature	All	Increase Increase by 10K	Increase Approximately Doubles
Concentration	All	Increase Doubling [C] of one reactant	Usually increases (unless zero order) Usually Exactly doubles (if first order
Light	Generally those involving reactions of mixtures of gases including halogens	Reactions in sunlight or UV	Very large increase
Particle Size	Reactions involving (s)&(l), or (s)&(g) or mixtures	Powdering the solid, resulting in large increase in surface area	Very large increase

Topic 6.2b: 6.2.5 – 6.2.7

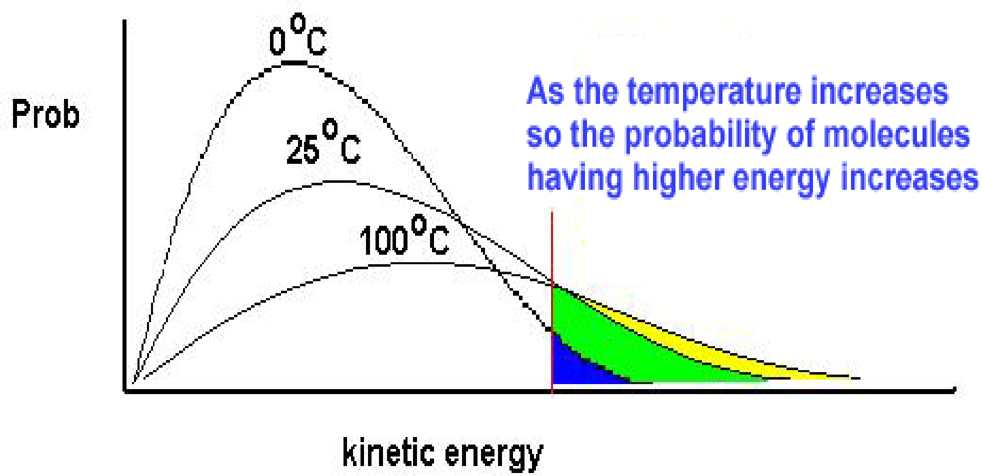
Next class we will discuss the Maxwell-Boltzmann, curves associated with M-B, and the effects of catalysts

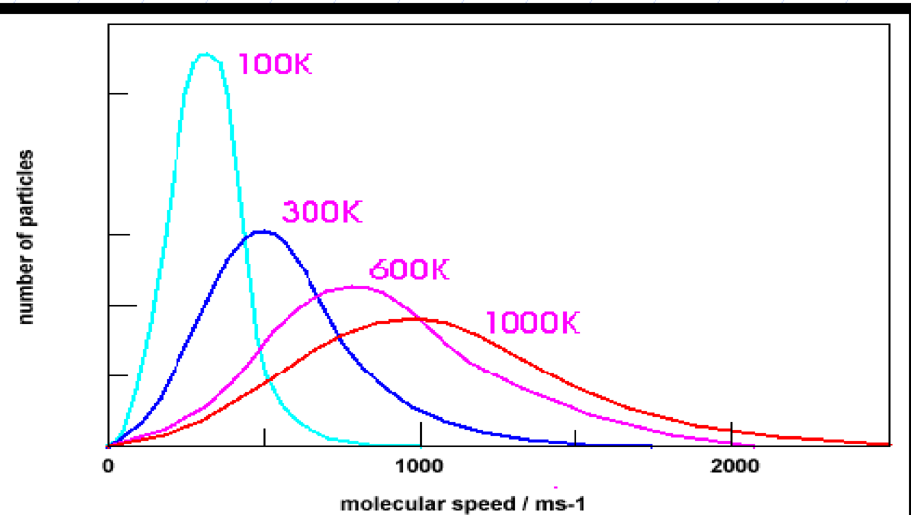
6.2.5 – Maxwell-Boltzmann Curve

- 6.2.5 Sketch and explain qualitatively the Maxwell–Boltzmann energy distribution curve for a fixed amount of gas at different temperatures and its consequences for changes in reaction rate. (3)
- Theoretical calculations and experimental measurements both suggest that the translational (and vibrational) kinetic energies of gas molecules in an ideal gas are distributed over a range known as a **Maxwell-Boltzmann distribution**
- Similar distributions of kinetic energies are present in the particles in solutions and liquids

6.2.5 – Maxwell-Boltzmann Curve

- The following curve shows the Maxwell-Boltzmann distribution of kinetic energies in a solution or gas at three different temperatures.
- The area under the curve is directly proportional to the total number of molecules and molecules containing energies within that range





6.2.5 – Temperature Effect on the Maxwell-Boltzmann Curve

- The **peak** of the curve moves to the right so the most likely value of kinetic energy for the molecules increases
- The **curve flattens** so the total area under it and, therefore, the total number of molecules remains constant
- The **area under the curve to the right of the activation energy**, E_a, increases. This means that at higher temperatures, a greater percentage of molecules have energies equal to or in excess of the activation energy, E_a.

6.2.5 – Effect of Temperature Change

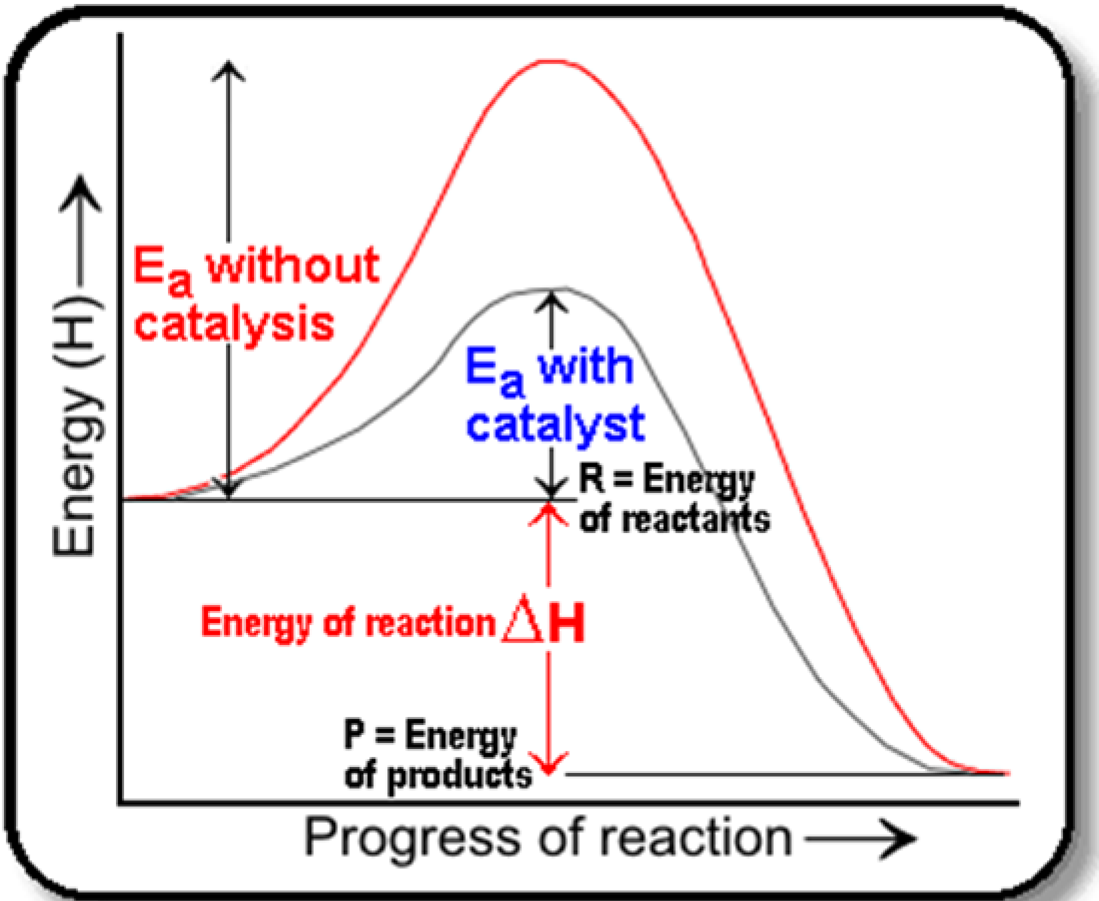
- The increased temperature raises the collision rate because average speeds of particles in the gas, liquid, or solution are increased
  - Small effect
  - Temperature +10^{o}C = 2% increase in collision rate
- The increased temperature raises the total energy that each molecule possesses and allows many new molecules to overcome the activation energy
  - Big effect
  - Temperature +10^{o}C = 100% increase in rate

6.2.6/7 – Effect of Catalysts

- 6.2.6 Describe the effect of a catalyst on a chem rxn
- 6.2.7 Sketch and explain Maxwell–Boltzmann curves for reactions with and without catalysts. (3)
- A **catalyst** is a substance that can increase the rate of reaction but remains chemically unchanged at the end of the reaction.
- Catalysts are important in many industrial processes, where they are frequently transition metals or their compounds
- Catalysts **increase** the rate of reaction by providing a new alternative pathway or **mechanism** for the reaction that has a lower activation energy

6.2.6 – Catalyst Energy Diagram

- The general enthalpy level diagram for a catalyzed and uncatalyzed exothermic reaction.



6.2.6/7 – Catalyst does not…

- Catalysts **do not** alter the position of equilibrium, they only increase the rate at which equilibrium is achieved.
  - The presence of a catalyst **does not** increase the yield or products
  - The equilibrium stays constant
  - Both the forward and reverse activation energies are lowered, increasing the rates in both directions
  - No effect on reactions that are not thermodynamically spontaneous. They do not alter enthalpy change, ΔH, or Gibbs free, ΔG.

6.2.6/7 – Catalyst Examples

- Biological catalysts are known as enzymes (proteins) and consist of those often associated with metal ions
- A substance that decreases the rate of reaction is called an **inhibitor**
- The 'anti-lock' compound, tetraethyl lead(IV), used to prevent ignition of 'leaded' petroleum vapor is and example of an inhibitor

6.2.6/7 – Catalyst Examples

- In chemical industry:
  - Finely divided iron in the Haber process for making ammonia and platinum in the Contact Process (Topic 07 – soon)
  - A complex organo-metallic catalyst, known as Ziegler-Natta catalyst, is used in the production of polymers from alkenes (Adv. Organic)
  - Solid MnO_2 (manganese (IV) oxide) acts as a catalyst to decompose hydrogen peroxide
    - $2H_2O_2(aq) \rightarrow 2H_2O + O_2(g)$
    - Insoluble MnO_2 can be filtered off after, washed and dried for reuse (since catalysts are not altered)

6.2.6/7 – Catalyst Examples

- Oxidation of potassium sodium tartrate by hydrogen peroxide solution to give a mixture of oxygen and carbon dioxide gases
  - Reaction is catalyzed by $CoCl_2$
  - As the experiment proceeds the pink color of the aqueous Co^{2+} ions changes to green (intermediate), before returning to pink indicating a regeneration of the catalyst.

6.2.6/7 – Homo/Heterogeneous Catalysts

- **Heterogeneous** catalyst:
  - This involves the use of a catalyst in a different phase from the reactants. Typical examples involve a **solid** catalyst with the reactants as either **liquids or gases**.
- **Homogeneous** catalyst:
  - This has the catalyst in the same phase as the reactants. Typically everything will be present as a gas or contained in a single liquid phase.

6.2.6/7 - Autocatalysis

- The reaction is catalyzed by one of its products.
- The oxidation of ethanedioic acid by manganate(VII) ions
- The reaction is very slow at room temperature. It is used as a titration to find the concentration of potassium manganate(VII) solution and is usually carried out at a temperature of about 60°C. Even so, it is quite slow to start with.
- The reaction is catalyzed by manganese(II) ions. There obviously aren't any of those present before the reaction starts, and so it starts off extremely slowly at room temperature. However, if you look at the equation, you will find manganese(II) ions amongst the products. More and more catalyst is produced as the reaction proceeds and so the reaction speeds up.

$$2MnO_4^- + 6H^+ + 5\begin{matrix}COOH\\ |\\ COOH\end{matrix} \longrightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$$